

Influence of Ge and Bi substitution on the magnetic and magnetocaloric properties of $\text{LaFe}_{11.4}\text{Si}_{1.6}$

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In this work, the magnetic and magnetocaloric properties of $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ ($x = 0.05, 0.1$ and 0.2) and $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x = 0, 0.1$ and 0.2) compounds have been investigated. X-ray results indicate that the samples with lower Ge and Bi contents mainly consist of the NaZn_{13} -type phase with a small amount of α -Fe impurity phase. The α -Fe impurity phase increases with increasing concentrations of Ge and Bi. The Curie temperature of the samples also increases slightly with increasing Ge and Bi contents. The spin-wave dispersion coefficient D , exchange constant J and average mean-square range of exchange interaction $\langle r^2 \rangle^{1/2}$ have been calculated. The increase in Curie temperature is attributed to an increase in the average Fe-Fe distance and ferromagnetic interactions. The peak values of the magnetic entropy change $[\Delta S_m]$ are found to decrease with increasing Ge and Bi contents. This is attributed to a change of the phase transition from first order to second order. The peak values of $[\Delta S_m]$ are 22.38 J/kg K for $\text{LaFe}_{11.4}\text{Si}_{1.6}$, 12.58 J/kg K for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and 14.25 J/kg K for $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ at a magnetic field of 6 T.

(Received March 10, 2010; accepted May 26, 2010)

Keywords: NaZn_{13} -type intermetallics compounds, Magnetocaloric effect, Magnetic entropy change, LaFeSi

1. Introduction

In the last few years, magnetic materials that show a large magnetocaloric effect (MCE) have been intensively studied. The interest in such materials is related to their possible practical application in magnetic refrigeration as an alternative to conventional vapour-cycle refrigeration [1-6]. Magnetic-refrigeration technology has several advantages over the gas-compression technique, such as compactness, high efficiency, low energy consumption and environmental safety.

Much attention has been paid to materials that have a first-order magnetic phase transition, because such compounds exhibit larger values of the magnetocaloric quantities than compounds undergoing second-order magnetic phase transitions [7-11]. Up to now, many materials with first-order magnetic phase transitions, such as $\text{Gd}_5\text{Si}_{4-x}\text{Ge}_x$ [12], MnAs [13], $\text{MnFeP}_{1-x}\text{As}_x$ [14], $\text{MnAs}_{1-x}\text{Sb}_x$ [15], and $\text{LaFe}_{13-x}\text{Si}_x$, have been found to exhibit a very large MCE [16, 17]. Among these materials, the cubic NaZn_{13} -type $\text{LaFe}_{13-x}\text{Si}_x$ compounds have attracted much attention due to the low cost of their raw materials and their lack of toxicity [18]. Previous investigations on $\text{LaFe}_{13-x}\text{Si}_x$ revealed that compounds with low Si concentration ($x < 1.7$) undergo a first-order magnetic phase transition from ferromagnetic (FM) to paramagnetic (PM) at the Curie temperature T_C and a field-induced itinerant electron metamagnetic transition from the PM to FM phase [19-25]. The large MCE is closely related to these phase transitions. The influence of substituting transition metals (Ni, Cu, Cr, V, Co) for Fe [26, 27] and rare-earth elements (Nd, Pr, Gd, Ce Er) for La [28-31] has also been studied in the cubic NaZn_{13} -type LaFeSi compounds.

But the effect of adding Ge and Bi on the MCE has not yet been reported. In this work, the influence of substituting Ge for Si and Bi for La on the MCE and T_C of LaFeSi compounds has been investigated.

2. Experimental

Polycrystalline $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ ($x = 0.05, 0.1$ and 0.2) and $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x = 0, 0.1$ and 0.2) samples were prepared by arc melting from high-purity metals under a pure argon atmosphere. The melting process was performed at 75 A current using an arc-melting furnace. The samples were turned over and melted several times to ensure their homogeneity. In our previous study, it was shown that an LaFeSi sample with cubic NaZn_{13} structure could be produced at high temperature with a shorter annealing time [32]. So, the resulting samples were sealed in a quartz tube under high vacuum, and annealed at 1473 K for 60 min to homogenize the material. The sealed samples were directly placed into the pre-heated furnace at 1473 K and were quenched in iced water after the annealing process.

The structures of the samples were investigated by an X-ray diffractometer (Rigaku-Radb) system. X-ray diffractograms were recorded with a powder diffractometer at room temperature using CuK_α radiation.

Magnetic measurements of the polycrystalline $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ ($x = 0.05, 0.1$ and 0.2) and $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x = 0, 0.1$ and 0.2) samples were performed using a Q-3398 (Cryogenic) magnetometer in the temperature range 150 to 250 K and a maximum magnetic field of 6 T was applied.

3. Results and discussion

Fig. 1 shows the room-temperature X-ray diffraction patterns of $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ compounds for $x=0, 0.05, 0.1$ and 0.2 . The results indicate that the sample with $x=0$ crystallizes in a single phase with a cubic NaZn_{13} structure. The samples with lower Ge content mainly consist of the cubic NaZn_{13} type phase and a small amount of α -Fe impurity phase. The amount of α -Fe impurity phase increases (observed at $2\theta = 44.7^\circ$) with increasing Ge concentration. The sample with a higher Ge content ($x=0.2$), mainly consists of the α -Fe and cubic NaZn_{13} -type phases, indicating that replacing Si with Ge is unfavourable for formation of the cubic NaZn_{13} -type phase. No tetragonal LaFeSi impurity phase is observed for any of the Ge concentrations. The lattice parameters obtained from the X-ray diffraction patterns are 11.466, 11.471, 11.474 and 11.477 Å for $x = 0, 0.05, 0.1$ and 0.2 , respectively. There is a small increase in the lattice parameters with increasing Ge content, because the ionic radius of Ge is larger than that of Si. The X-ray diffraction patterns of $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ compounds for $x = 0, 0.1$ and 0.2 show the same properties as $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$.

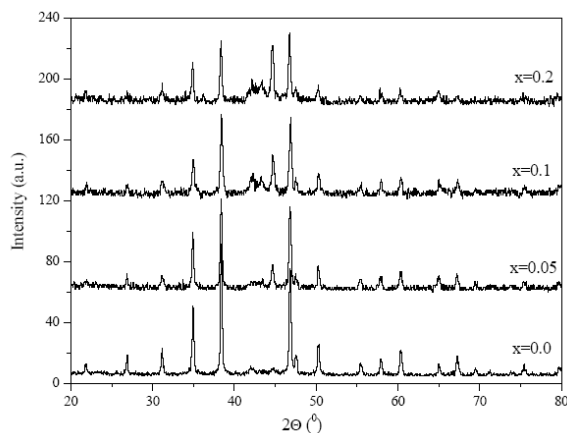


Fig. 1. XRD patterns of $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ compounds for $x = 0, 0.05, 0.1$ and 0.2 .

Fig. 2 shows the temperature dependence of magnetization for $\text{LaFe}_{11.4}\text{Si}_{1.6}$ and $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ samples in an applied magnetic field of 0.1 T. The Curie temperatures T_c , defined as the temperature at which $|dM/dT|$ is a maximum, are measured to be 193 K for $\text{LaFe}_{11.4}\text{Si}_{1.6}$, 200 K for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and 205 K for $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ samples at 0.1 T magnetic field. The Curie temperatures of Ge- and Bi-doped samples are slightly higher than that of the undoped sample. For different Ge and Bi concentrations, the Curie temperatures increase with increasing doping level from 193 K for $x = 0$ to 202 K for $x = 0.2$ in Ge-doped samples and 193 K for $x = 0$ to 210 K for $x=0.2$ in Bi-doped samples. This indicates that substitution of Ge or Bi appears to improve the structural stability and, in consequence, the ferromagnetic interactions in the sample. The relatively large magnetization above T_c is attributed to the presence of the strongly ferromagnetic α -Fe impurity phase, which

is clearly observed in the X-ray diffraction patterns of the samples.

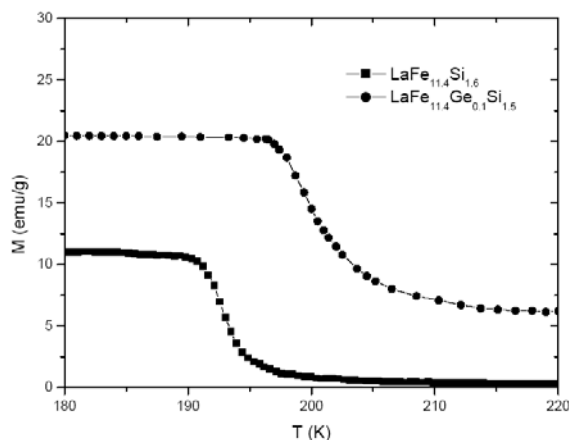


Fig. 2. Temperature dependence of magnetization for $\text{LaFe}_{11.4}\text{Si}_{1.6}$ and $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ samples in an applied magnetic field of 0.1 T.

Shen et al. [33] have concluded that the Curie temperatures of rare-earth (R) and transition-metal (T) compounds are jointly determined by the T–T, R–T and R–R interactions. In general, the T–T interaction is the strongest, while the R–R exchange is the weakest. In $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ and $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$, Si and La are replaced by the non-magnetic Ge and Bi, respectively. Due to the non-magnetic properties of the doping elements, R–T and R–R exchange interactions are not expected. In this case, the magnetic properties of $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ and $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ compounds arise mainly from Fe–Fe (T–T) exchange interactions. Doping with Ge and Bi does not change the number of Fe atoms or, in consequence, the number of Fe–Fe pairs. The change in strength of the magnetic interactions and Curie temperature with Ge and Bi doping could be attributed to the change in average Fe–Fe exchange-interaction distances. Liu et al. [34] showed that the average Fe–Fe distance plays a critical role in the exchange interaction and T_c value in $\text{LaFe}_{13-x}\text{Si}_x$ compounds. They also showed that increasing the average Fe–Fe distance enhances the ferromagnetic exchange interaction and the value of T_c .

In order to understand the effect of the doping elements on magnetic interactions in the $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ and $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ compounds, the low-temperature magnetization data were fitted to the following equation, called spin-wave approximation [35, 36]:

$$M(T) = M(0) \left[1 - BT^{\frac{3}{2}} - CT^{\frac{5}{2}} \right] \quad (1)$$

where $M(0)$ is the magnetization at zero temperature, and B and C are the Bloch coefficients. They are related to the spin-wave excitation through the relations [35, 36]

$$B = 2.612 \left(\frac{g \mu_B}{M(0)} \right) \left(\frac{k_B}{4\pi D} \right)^{3/2} \quad (2)$$

$$C = 1.341 \left(\frac{g \mu_B}{M(0)} \right) \left(\frac{k_B}{4\pi D} \right)^{5/2} \frac{3}{4} \pi \langle r^2 \rangle \quad (3)$$

where g is the Lande factor, μ_B is the Bohr magneton, k_B is the Boltzmann constant, D is the spin-wave stiffness constant and $\langle r^2 \rangle$ is the mean-square range of the exchange interaction, defined as

$$\langle r^2 \rangle = 1.947 \left(\frac{16}{3k_B} \right) \left(\frac{CD}{B} \right) \quad (4)$$

The Bloch coefficients B and C were calculated by fitting Eq. (1) to the experimental $[(M(0)-M(T))/M(0)]T^{3/2}-T$ curves at low temperatures. The spin-wave dispersion coefficients D were calculated using Eq. (2). The mean-square range of exchange interactions was calculated from Eq. (4). The spin-wave dispersion coefficient D is closely related to the degree of ferromagnetic exchange interaction, given by

$$J_{exc} = \frac{M(0)D}{2g\mu_B} \quad (5)$$

The strength of the exchange interaction was calculated from Eq. (5). The calculated parameters are listed in Table 1 for LaFe_{11.4}Si_{1.6-x}Ge_x and Table 2 for La_{1-x}Bi_xFe_{11.4}Si_{1.6}. The Bloch coefficients B and C decrease with increasing Ge and Bi contents. It is evident from Tables 1 and 2 that the spin-wave dispersion coefficients D increase with the level of Ge and Bi doping. This increase of D with increasing doping (Ge and Bi) concentration means the ferromagnetic state has become stabilized. We have calculated the average mean-square range of exchange interaction $(\langle r^2 \rangle)^{1/2}$ and the exchange

constant (J) using Eqs. (4) and (5), respectively. As can be seen in Tables 1 and 2, the average mean square range of exchange interactions is found to increase with increasing doping level, which indicates that there is an increase in the average Fe-Fe exchange interaction distance. As discussed above, such an increase causes an increase in thermal stabilization of the ferromagnetic exchange interaction as well as an increase in T_c . Fig. 3 shows the variation of Curie temperature and ferromagnetic exchange interaction with doping level. The Curie temperature and exchange interaction for La_{1-x}Bi_xFe_{11.4}Si_{1.6} samples are larger than those of LaFe_{11.4}Si_{1.6-x}Ge_x samples. In previous studies, it was concluded that in NaZn₁₃-type compounds the magnetic interactions and Curie temperature are very sensitive to the composition and Si/Fe ratio [7, 29, 34]. In LaFe_{11.4}Si_{1.6-x}Ge_x alloy Si atoms are replaced by Ge atoms. The decrease in Si content with increasing Ge results in a decrease in Si/Fe ratio. A change in the local atomic surroundings of Fe weakens the exchange interaction and lowers the Curie temperature compared with those of La_{1-x}Bi_xFe_{11.4}Si_{1.6} alloys.

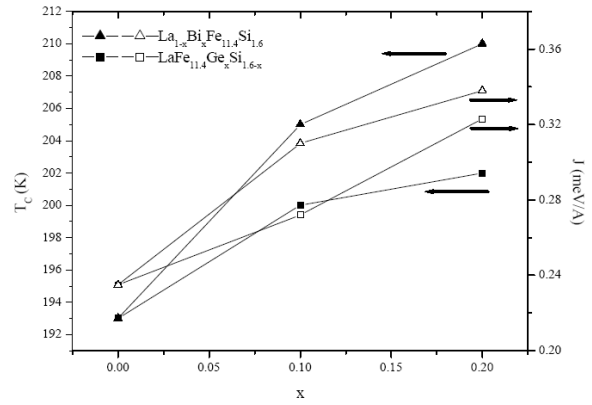


Fig. 3 Variation of Curie temperature and exchange interaction as a function of x for LaFe_{11.4}Si_{1.6-x}Ge_x and La_{1-x}Bi_xFe_{11.4}Si_{1.6} samples.

Table 1. Bloch coefficients (B and C), spin-wave stiffness constant (D), exchange interaction (J), mean-square range of exchange interaction $(\langle r^2 \rangle)^{1/2}$ and Curie temperature (T_c) for LaFe_{11.4}Si_{1.6-x}Ge_x alloys as a function of x .

x	$B(K^{-3/2}) \times 10^{-4}$	$C(K^{-5/2}) \times 10^{-6}$	$D(\text{meV}\text{\AA}^2)$	$J(\text{meV}/\text{\AA})$	$\langle r^2 \rangle^{1/2}(\text{\AA})$	T_c (K)
0	9.6	2.81	11.78	0.235	1.950	193
0.1	7.8	2.42	12.25	0.272	2.139	200
0.2	5.5	1.66	12.90	0.323	2.180	202

Table 2. Bloch coefficients (B and C), spin-wave stiffness constant (D), exchange interaction (J), mean-square range of exchange interaction $(\langle r^2 \rangle)^{1/2}$ and Curie temperature (T_c) for La_{1-x}Bi_xFe_{11.4}Si_{1.6} alloys as a function of x .

x	$B(K^{-3/2}) \times 10^{-4}$	$C(K^{-5/2}) \times 10^{-6}$	$D(\text{meV}\text{\AA}^2)$	$J(\text{meV}/\text{\AA})$	$\langle r^2 \rangle^{1/2}(\text{\AA})$	T_c (K)
0	9.6	2.81	11.78	0.235	1.950	193
0.1	6.1	1.83	13.43	0.310	2.260	205
0.2	5.3	1.71	14.76	0.338	2.283	210

Fig. 4 shows the variation of magnetization as a function of applied magnetic field at different temperatures for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.05}$. The $M(H)$ curves show ferromagnetic-like behavior below the Curie temperature. The magnetization curves above T_c exhibit a sharp change typical of first-order transition behaviour, as in the case of the parent compound $\text{LaFe}_{11.4}\text{Si}_{1.6}$. Fig. 5 shows the $M(H)$ curves above T_c for $\text{LaFe}_{11.4}\text{Si}_{1.6}$, $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ samples. The sharp change of magnetization with magnetic field disappears for the samples doped with Ge and Bi. In previous studies, it was concluded that the disappearance of this sharp change of magnetization may be caused by the existence of a relatively large amount of α -Fe impurity phase in the samples, this impurity phase being strongly ferromagnetic. The increase of α -Fe phase in the sample suppresses the magnetic behaviour of the main phase near the transition temperature. This effect is also clearly seen in the $M(T)$ curves (Fig. 2). While the magnetization drops sharply around T_c for $\text{LaFe}_{11.4}\text{Si}_{1.6}$, which is evidence of a first-order transition, the magnetization variation is very slow for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ samples due to the existence of the strongly ferromagnetic α -Fe phase. The magnetic entropy, which is associated with the MCE, can be calculated from the isothermal magnetization curves (Fig. 4) under the influence of a magnetic field. According to classical thermodynamics, the magnetic entropy change ΔS_m produced by the variation of a magnetic field from 0 to H_{\max} is given by

$$\Delta S_m(T, H) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (6)$$

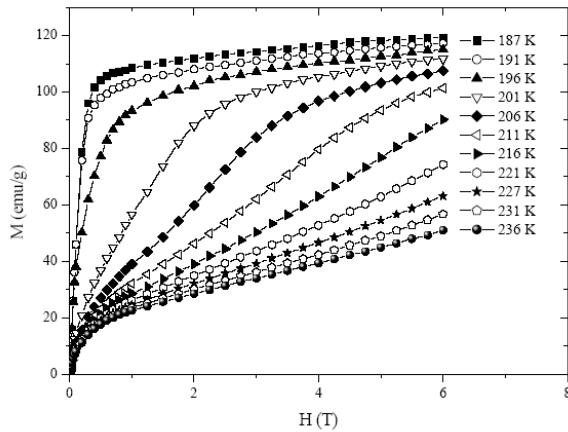


Fig. 4. Isothermal magnetization curves for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.05}$ at various temperatures.

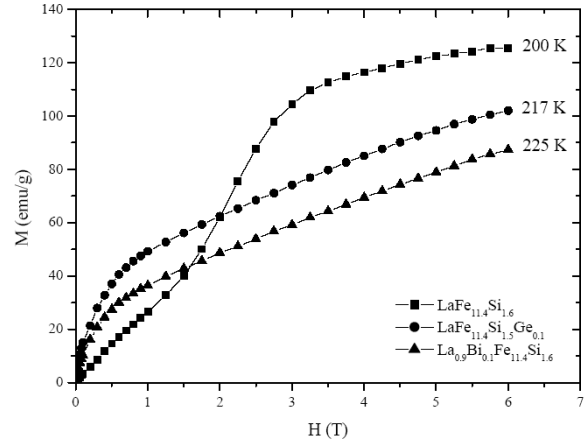


Fig. 5. Isothermal magnetization curves for $\text{LaFe}_{11.4}\text{Si}_{1.6}$, $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ samples above their Curie temperatures.

The evaluation of the magnetic entropy change ΔS_m requires numerical approximation of the integral in Eq. (6). The usual method is to use isothermal magnetization measurements at small discrete field intervals. Then ΔS_m can be approximated from Eq. (6) by

$$|\Delta S_m| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H \quad (7)$$

where M_i and M_{i+1} are the experimental values of the magnetization at T_i and T_{i+1} , respectively. Using Eq. (7) and the experimental $M(H)$ curves at various temperatures, the magnetic entropy change when the magnetic field is varied can be calculated. Figs 6–8 show the magnetic entropy change at various magnetic fields for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.05}$, $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ samples, respectively. The peak values of $|\Delta S_m|$ are 18.53 J/kg K for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.05}$ and 14.25 J/kg K for $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ at 6 T magnetic field. These values are lower than that of the parent $\text{LaFe}_{11.4}\text{Si}_{1.6}$ sample (22.38 J/kg K at 6 T magnetic field). Calculations for other Ge and Bi concentrations show that while the peak temperatures shift upwards, the peak values of $|\Delta S_m|$ decrease with increasing doping level. As can be seen from Figs. 6 and 7, $|\Delta S_m|$ decreases from 18.53 J/kg K for $x = 0.05$ to 8.33 J/kg K for $x = 0.2$ at 6 T magnetic field in the $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ sample. The same property has been observed for the $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ sample. As discussed above, the increase in peak temperature with increasing Ge and Bi contents is related to an increase in ferromagnetic exchange interaction. The decrease of magnetic entropy change with increasing Ge and Bi contents is closely related to the nature of the magnetic phase transition.

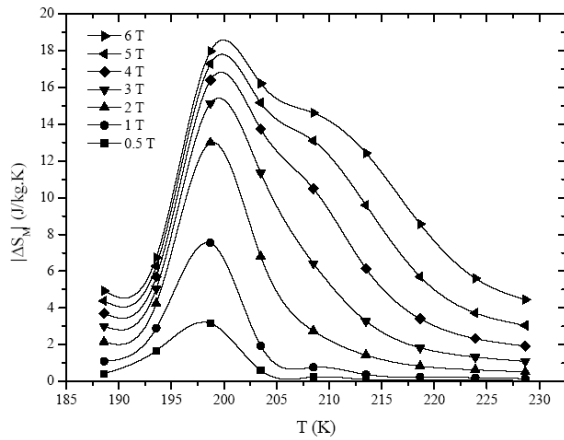


Fig. 6. Magnetic entropy change of $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.05}$ at various magnetic fields.

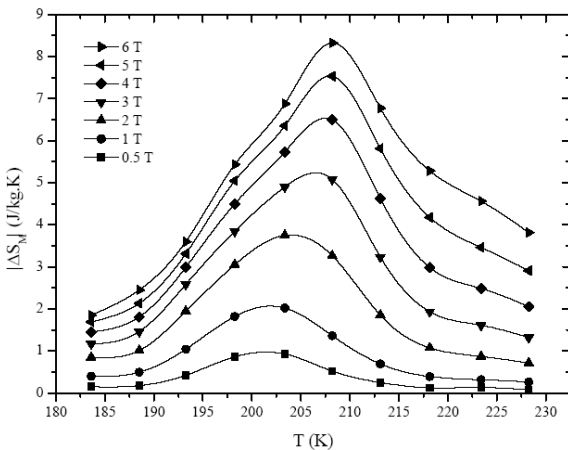


Fig. 7. Magnetic entropy change of $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ at various magnetic fields.

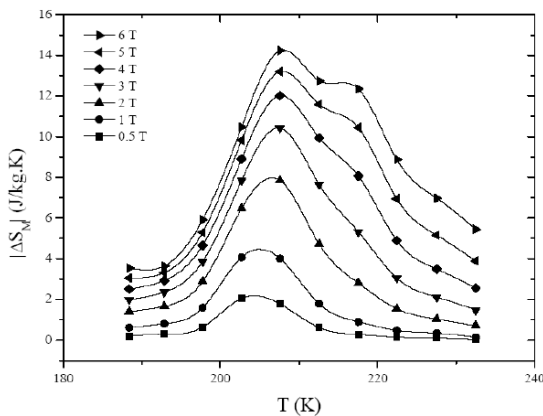


Fig. 8. Magnetic entropy change of $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ at various magnetic fields.

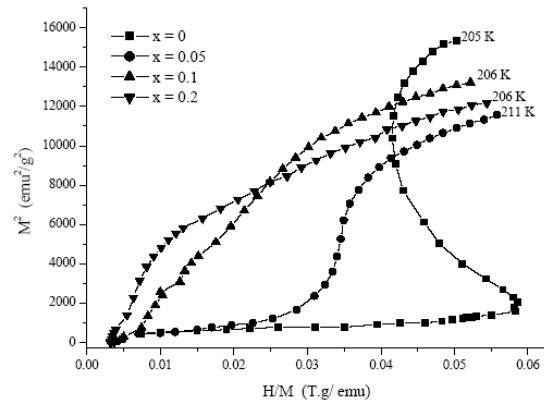


Fig. 9. Arrott plots of $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ for $x = 0, 0.05, 0.1$ and 0.2 above their Curie temperatures.

By plotting H/M versus M^2 in the critical region, which is called an Arrott plot, the slope of the curves denotes whether the magnetic transition is of first or second order. It can be deduced that if all the curves have a positive slope, the magnetic transition is second order. On the other hand, if some of the curves show a negative slope at same point, then the magnetic transition is first order. Fig. 9 shows the Arrott plots of $\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ for $x = 0, 0.05, 0.1$ and 0.2 above their Curie temperatures. The negative slope of the plot for the parent $\text{LaFe}_{11.4}\text{Si}_{1.6}$ alloy clearly shows the first-order nature of the magnetic phase transition. The occurrence of an S-shaped curve (inflection point) for the $x = 0.05$ sample indicates that the phase transition is still first order. For higher doping concentrations ($x = 0.1$ and 0.2), the nearly straight-line form of the H/M versus M^2 curves reveals that the magnetic phase transition has changed to second order. This disappearance of the first-order phase transition in the $x = 0.1$ and 0.2 samples may be caused by the existence of a relatively large amount of ferromagnetic α -Fe phase. This effect is also clearly seen in the $M(T)$ and $M(H)$ curves. As a consequence, the decrease of the MCE with increasing doping level can be explained by the fact that substituting Ge for Si or Bi for La transforms the nature of the magnetic phase transition from first to second order.

4. Conclusions

$\text{LaFe}_{11.4}\text{Si}_{1.6-x}\text{Ge}_x$ ($x = 0.05, 0.1$ and 0.2) and $\text{La}_{1-x}\text{Bi}_x\text{Fe}_{11.4}\text{Si}_{1.6}$ ($x = 0, 0.1$ and 0.2) samples were prepared by arc melting and their magnetic and magnetocaloric properties investigated. X-ray results indicated that the samples with lower Ge and Bi contents mainly consist of the NaZn_{13} -type phase and a small amount of α -Fe impurity phase. The α -Fe impurity phase increases with increasing Ge and Bi concentrations. For higher Ge and Bi doping levels, the samples mainly consist of α -Fe and cubic NaZn_{13} -type phases. The samples were magnetically characterized at various temperatures and magnetic fields. It was observed that the Curie temperatures of the samples increase slightly with increasing Ge and Bi contents. The

spin-wave dispersion coefficient D , which is closely related to the degree of the ferromagnetic exchange interaction, the exchange constant J and the average mean-square range of the exchange interaction $(\langle r^2 \rangle)^{1/2}$, were calculated. The increase in Curie temperature with increasing Ge and Bi contents has been attributed to an increase of the Fe–Fe distance and ferromagnetic interactions. The peak values of $|\Delta S_m|$ are 22.38 J/kg K for $\text{LaFe}_{11.4}\text{Si}_{1.6}$, 12.58 J/kg K for $\text{LaFe}_{11.4}\text{Si}_{1.5}\text{Ge}_{0.1}$ and 14.25 J/kg K for $\text{La}_{0.9}\text{Bi}_{0.1}\text{Fe}_{11.4}\text{Si}_{1.6}$ at 6 T magnetic field. The decrease of the magnetocaloric effect with increasing doping level is explained by the fact that substituting Ge for Si or Bi for La transforms the nature of the magnetic phase transition from first to second order. As a consequence, a slight enhancement of Curie temperature is observed in Ge- and Bi-doped compounds, while the magnetic entropy change decreases considerably with increasing doping level due to this change of phase transition from first to second order.

Acknowledgment

This work was supported by Inonu University Research Fund under Project Number 2009/31.

References

- [1] O. Tegus, E. Brück, K. H. J. Buschow, F. R. de Boer, *Nature* **415**, 150 (2002).
- [2] V. K. Pecharsky, K. A. Gschneider Jr, *Phys. Rev. Lett.* **78**, 4494 (1997).
- [3] V. K. Pecharsky, K. A. Gschneider Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
- [4] A. M. Tishin, Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications*, first ed., Institute of Physics, Bristol, Philadelphia (2003).
- [5] H. Gencer, S. Atalay, H. I. Adiguzel, V. S. Kolat, *Physica B* **357**, 326 (2005).
- [6] S. Atalay, H. Gencer, V. S. Kolat, *J. Non-Crystal. Solids* **351**, 2373 (2005).
- [7] Y. Zhu, K. Xie, X. Song, Z. Sun, W. Lv, *J. Alloys and Compounds* **392**, 20 (2005).
- [8] A. M. Tishin, Y. I. Spichkin, *The Magnetocaloric Effect and Its Applications*, Institute of Physics Publishing Ltd., Bristol, 2003.
- [9] H. Gencer, V. S. Kolat, S. Atalay, *J. Alloys and Compounds* **422**, 40 (2006).
- [10] A. M. Gomes, M. S. Reis, I. S. Oliveira, A. P. Guimaraes, A. Y. Takeuchi, *J. Magn. Magn. Mater.* **242–245**, 870 (2002).
- [11] V. S. Kolat, T. Izgi, O. A. Kaya, H. Gencer, N. Bayri, S. Atalay, *J. Non-Crystal. Solids* **322**, 427 (2010).
- [12] V. K. Pecharsky, K. A. Gschneider Jr, *Appl. Phys. Lett.* **70**, 3299 (1997).
- [13] H. Wada, T. Morikawa, K. Taniguchi, T. Shibata, Y. Yamada, Y. Akishige, *Physica B* **328**, 114 (2003).
- [14] O. Tegus, E. Brück, K. H. J. Buschow, F. R. de Boer, *Nature* **415** (2002) 450,
- [15] H. Wada, Y. Tanabe, *Appl. Phys. Lett.* **79**, 3302 (2001).
- [16] F. X. Hu, B. G. Shen, R. J. Sun, Z. H. Cheng, G. H. Rao, X. X. Zhang, *Appl. Phys. Lett.* **78**, 3675 (2001).
- [17] S. Fujieda, A. Fujita, K. Fukamichi, *Appl. Phys. Lett.* **81**, 1276 (2002).
- [18] Y. Zhu, K. Xie, X. Song, Z. Sun, W. Lv, *J. Alloys and Compounds* **392**, 20 (2005).
- [19] F. X. Hu, B. G. Shen, R. J. Sun, X. X. Zhang, *Chin. Phys.* **9**, 550 (2000).
- [20] B. F. Yu, Q. Gao, B. Zhang, X. Z. Meng, Z. Chen, *Int. J. Refrigeration* **26**, 622 (2003).
- [21] Y. F. Chen, F. Wang, B. G. Shen, F. X. Hu, J. R. Sun, G. J. Wang, Z. H. Cheng *J. Phys: Condens. Matter* **15**, L161 (2003).
- [22] A. Fujita, S. Fujieda, K. Fukamichi, Y. Yamazaki, Y. Iijima, *Trans. Mater. Res. Soc. Japan* **26**, 219 (2001).
- [23] S. Fujieda, A. Fujita, K. Fukamichi, Y. Yamazaki, Y. Iijima, *Appl. Phys. Lett.* **79**, 653 (2001).
- [24] F. Wang, Y. F. Chen, G. J. Wang, B. G. Shen, *J. Phys. D* **36**, 1 (2003).
- [25] Y. F. Chen, F. Wang, B. G. Shen, J. R. Sun, G. J. Wang, F. X. Hu, Z. H. Cheng, T. Zhu, *J. Appl. Phys.* **93**, 6981 (2003).
- [26] A. K. Pathak, P. Basnyat, I. Dubenko, S. Stadler, N. Ali, *J. Magn. Magn. Mater.* **322**, 692 (2010).
- [27] A. T. Saito, T. Kobayashi, H. Tsuji, *J. Magn. Magn. Mater.* **310**, 2808 (2007).
- [28] S. Fujieda, A. Fujita, K. Fukamichi, N. Hirano, S. Nagaya, *J. Alloys Compds.* **408–412**, 1165 (2006).
- [29] M. Balli, D. Fruchart, D. Gignoux, M. Rosca, S. Miraglia, *J. Magn. Magn. Mater.* **312**, 43 (2007).
- [30] D. T. Kim Anh, N. P. Thuy, N. H. Duc, T. T. Nhien, N. V. Nong, *J. Magn. Magn. Mater.* **262**, 427 (2003).
- [31] A. Fujita, K. Fukamichi, *IEEE Trans. Magn.* **35**, 1796 (1999).
- [32] V. S. Kolat, T. Izgi, H. Gencer, A. O. Kaya, N. Bayri, S. Atalay, *J. Optoelectron. Adv. Mater.* **11**, 1106 (2009).
- [33] J. Shen, B. Gao, Q. Y. Dong, Y. X. Li, F. X. Hu, J. R. Sun, B. G. Shen, *J. Phys. D: Appl. Phys.* **41**, 245005 (2008).
- [34] X. B. Liu, Z. Altounian, D. H. Ryan, *J. Phys.: Condens. Matter* **15**, 7385 (2003).
- [35] K. S. Kim, S. C. Yu, *J. Korean Phys. Soc.* **24**, 73 (1991).
- [36] M. Konc, P. Spisak, P. Kollar, P. Sovak, O. Dusa, *IEEE Trans. on Magnetism* **30**, 524 (1994).

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